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EFFICIENT MATHEMATICAL MODELING OF AN INTEGRATED HIGH LEVEL WASTE PROCESSING COMPLEX

WASTE MANAGEMENT
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An integrated computational tool named the Production Planning Model (ProdMod) has been developed to simulate the operation of the entire high level waste complex (HLW) at the Savannah River Site (SRS) over its full life cycle. ProdMod is used to guide SRS management in operating the waste complex in an economically efficient and environmentally sound manner. SRS HLW operations are modeled using coupled algebraic equations. The dynamic nature of plant processes is modeled in the form of a linear construct in which the time dependence is implicit. Batch processes are modeled in discrete event-space, while continuous processes are modeled in time-space. The ProdMod methodology maps between event-space and time-space such that the inherent mathematical discontinuities in batch process simulation are avoided, without sacrificing any of the necessary detail in the batch recipe steps. Modeling the processes separately in event- and time-space using linear constructs, and then coupling the two spaces, *has accelerated the speed of simulation compared to a typical dynamic simulation. The ProdMod simulator models have been validated against operating data and other computer codes. Case studies have demonstrated the usefulness of the ProdMod simulator in developing strategies that demonstrate significant cost savings in operating the SRS HLW complex and in verifying the feasibility of newly proposed processes.*

I. INTRODUCTION

The United States Department of Energy (DOE) manages millions of cubic meters of nuclear waste that has been generated during the last 50 years of operations, mostly related to the nation's defense activities. The total radioactivity in DOE managed waste is about 1 billion curies, with 94% of the activity attributed to high level waste (HLW). The DOE has started processing this HLW to transform it into a permanent waste disposal form. It is expected to take several decades to process all the wastes. Waste processing operations involve many highly interrelated facilities, each facility performing specific process functions. A state of the art computational tool can usefully guide the efficient execution of these decades-long process operations. This paper discusses the development of such a computational tool: ProdMod, the Production Planning Model.

The defense HLW is located at three different sites: the Hanford Site, the Idaho National Engineering and Environmental Laboratory (INEEL), and the Savannah River Site (SRS). At the SRS, 120,000 cubic meters of HLW are stored, representing 490 million curies of activity. Many waste processing operations are underway at different facilities at this site, and some new operations are in the process of coming on-line soon. At the SRS, the processing of HLW into borosilicate glass for final disposal form began in early 1996. The SRS was the first site in the United States where routine processing of radioactive wastes into a glass form took place. To support efficient waste processing at the SRS, a strategic modeling tool has been developed using a commercially available software package in a novel fashion. The objective was to develop a fast running computational tool for the integrated simulation of waste processing operations in general. The resulting tool simulates the dynamic response of all SRS HLW facilities in an integrated fashion for the entire life span of the complex. To achieve rapid turn-around, the computational tool models the waste processing operations and facilities in a pseudo-dynamic form using solely algebraic equations. A novel mapping technique is used to connect the batch processes modeled in discrete event-space with the continuous processes modeled in time-space.

A brief background of defense nuclear waste is given in Section II. A description of the SRS HLW processing operations, along with the plant facilities, is provided in Section III. The modeling methodology is discussed in Section IV, followed by model validations in Section V. The results of several studies are presented in Section VI. Additional discussion and conclusions are provided in Section VII.

II. BACKGROUND OF DEFENSE NUCLEAR WASTE

As of 1997 data,[1] the DOE manages 36 million cubic meters of waste. About 68% of that volume is due to nuclear weapons program activities, and the remaining 32% to non-weapons activities. This waste is categorized into seven different forms as defined by different Orders and Acts of the United States Federal Government. These are: 1) High Level Waste, 2) Transuranic Waste, 3) Low Level Waste, 4) Mixed Low Level Waste, 5) 11e(2) Byproduct Material, 6) Hazardous Waste, and 7) Other Waste. By waste volume category, 89% is attributed to 11e(2)-byproduct material, 9% is low level waste, and the remaining waste categories comprise the remaining 2%. The total radioactivity is 1.01 billion curies, with 89% of it attributed to weapons programs and the remaining 11% to non-weapons activities. Most of the radioactivity is in the high level waste form (94%), with 5% in low level waste, and only about 1% in the remaining waste categories. Hazardous waste does not have any radioactivity, and the DOE does not store it for a significant length of time. The stored volumes of the six other waste categories are given in Table I.

By virtue of the definition of high level waste in the Nuclear Waste Policy Act (10CFR, Part 60) and in the DOE Order 5820.2A, all HLW is attributed to chemical separations. All HLW is located at four sites: primarily defense wastes at the Hanford Site, the SRS, and the INEEL; and non-defense wastes at the West Valley Demonstration Project. A small portion of the HLW at Hanford and the SRS, and all of it at West Valley, is attributed to non-weapons programs. The distribution of waste volume and the curie content in HLW among four sites are shown in Table II. The activity and the dominant radionuclides of the HLW at four different time horizons are given in Table III. Cs^{137} and Sr^{90} contribute almost 99% of the HLW activity, with half lives about 30 years. Hence, most of the radioactivity will decay within the first 100 years. The HLW containing 55 million curies is yet to be categorized, and thus not included in Table III. The HLW at the SRS and the Hanford Site consists of alkaline supernate, saltcake, and sludge.[2,3,4] The volume of HLW at the SRS is only about half that at the Hanford Site, but it contains about one and one-half times the radioactivity. The Hanford tank waste is less radioactive because much of the radioactive Cs and Sr has been removed and concentrated in capsules. Moreover, the Hanford waste is older and has had more time to decay. The activities of waste at the SRS and in the Hanford tanks are on average 4,000 Ci/m^3 and 800 Ci/m^3, respectively. The Hanford Site has accumulated 208,000 m^3 (54.7 million gallons) of HLW in its 177 underground tanks (28 double shell and 149 single shell) from its defense nuclear operations over about 50 years. Of the total wastes, supernate, sludge, and saltcake account for 15.6, 14.2, and 24.9 million gallons, respectively. Most of the supernate has been pumped out of the single shell tanks. Currently, the single shell tanks contain mainly sludge and saltcake. At the Hanford Site, the Tank Farm evaporators are the only waste processing operations in place. The evaporators drive off excess water and concentrate HLW into crystalline saltcake, reducing its size and mobility. The HLW at the INEEL consists of acidic liquid and calcined solids. The acidic liquid is stored in underground tanks and its activity is 300 Ci/m^3. The calcine is an interim solid waste form, stored in bins, made by processing the liquid waste. The average activity of calcined bins is about 12,000 Ci/m^3. The vitrification of HLW at the Hanford Site and the INEEL is now in the planning stage. The HLW at the West Valley Demonstration Project consists of alkaline liquid, sludge, and ion-exchange resin. The HLW at West Valley is similar to that at the INEEL. The activity of liquid and solid waste at West Valley is about 1,700 Ci/m^3 and 150,000 Ci/m^3, respectively. The reprocessing of commercial nuclear fuels from 1966 to

1972 generated this waste. The vitrification of HLW at West Valley into glass form was started in July 1996.

Transuranic waste (TRU) as defined in the DOE Order 5820.2A as waste that is not HLW, contains alpha-emitting transuranic elements with half-lives greater than 20 years, and whose combined activity level is at least 100 nanocuries/gm at the time of assay. The primary radionuclides present in TRU waste include Pu^{239}, Pu^{240}, Pu^{241}, Pu^{238}, Pu^{242}, Am^{241}, Cm^{244}, Sr^{90}, Y^{90}, Cs^{137}, Ba^{137}, and Co^{60}. Most TRU waste is the result of the weapons production process and contains plutonium. About two-thirds of the TRU waste managed by the DOE has been disposed of, and the remaining one-third is in storage. The waste in storage will be disposed per DOE plan at the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico.

The low level waste (LLW) is defined in the DOE Order 5820.2A and is composed of all radioactive waste not classified as HLW, TRU waste, spent nuclear fuel, or 11e(2) byproduct material. The LLW comes from many sources (such as chemical separations, radioactive material handling facilities, nuclear components fabrication, pretreatment of HLW, environmental restoration, facility decommissioning, handling and treatment of TRU and mixed LLW) and is composed of a wide variety of radionuclides similar to those in TRU waste. Of all LLW managed by the DOE, about 85% is from weapons production. The LLW has been stored at 19 DOE sites, is currently being disposed of after treatment at six sites, and had been buried at eight DOE sites in the past.

The byproduct material from initial milling and refining of uranium ore constitute 11e(2) byproduct material as defined by law, under Section 11e(2) of the Atomic Energy Act (AEA) as amended by Title II of the Uranium Mill Tailing Radiation Control Act of 1978. The DOE manages approximately 32 million cubic meters of 11e(2) byproduct material, and about 65% is attributed to nuclear weapons production. The vast majority of 11e(2) byproduct material is composed of homogenous sand- or clay-like tailings, still containing most of the original radioactivity. The radioactivity of mill tailings is about 1,000 picocurie/gm, and the radioactivity comes from U^{230}, Th^{230}, Ra^{226}, and the daughter products of Ra^{226} decay.

The mixed low level waste contains hazardous waste subject to the Resource Conservation and Recovery Act (RCRA), and source, special nuclear, or byproduct material subject to the AEA. The mixed waste was formally defined by statute in 1992. The DOE manages about 146,000 cubic meters of mixed low level waste, and 69% is attributed to weapons production activities. The radionuclides in mixed low level waste are similar to those in low level waste. The mixed low level waste is generated during a broad spectrum of processes and activities including equipment maintenance, material production, cleaning, environmental restoration, facility deactivation, decommissioning, the treatment or handling of other waste. The mixed low level waste has been generated or stored at approximately 40 sites, and those from weapons production is managed at 18 sites.

Hazardous waste as defined under RCRA does not contain a radioactive component but has to meet the definition of a solid waste. The DOE stores and characterizes waste to comply with RCRA regulation and can easily release it to the private sector for treatment and disposal.

This waste is not considered a legacy from nuclear weapons production because no long term monitoring or management of the waste by the DOE is expected.

Other wastes include: 1) Polychlorinated Biphenyl (PCB)s and PCBs mixed radioactive waste subject to Toxic Substance Control Act (TSCA) but not subject to RCRA, 2) asbestos and low level waste asbestos not subject to RCRA, and 3) 11e(2) byproduct material mixed with a hazardous waste subject to RCRA. The DOE manages about 79,000 m^3 other waste at 30 sites, including 19 weapons production sites.

III. DESCRIPTION OF SRS HLW COMPLEX

The ProdMod computational tool discussed in this paper has been developed to simulate the SRS HLW complex, an overview of which is given in this section. The SRS has accumulated 127,000 m^3 (33.4 million gallons) of HLW in its 51 storage tanks from 40+ years' operation in support of the nation's nuclear defense programs. About 15.4 million gallons of the waste is in salt solution form called supernate, containing a variety of salts dominated by $NaNO_3$, NaOH, $NaNO_2$, and KNO_3. The waste in crystalline solid form called saltcake, created from supernate by evaporating excess water, accounts for 14.5 million gallons of the waste. Virtually all of the radioactivity in the supernate and saltcake is Cs^{137}. The remaining 3.5 million gallons of waste is called sludge, characterized as a supernate layer in which suspended insoluble solid particles are settled at the bottom of the tank. The sludge is mainly composed of oxides and hydroxides of Al, Fe, Ni, and Mn. The sludge contains about two-thirds of the radionuclides, primarily Sr^{90}.

The mission of the HLW program at the SRS is to receive and store these wastes in a safe and environmentally sound manner, and to convert the wastes into forms suitable for final disposal. The final forms are: borosilicate glass to be sent to a Federal Repository; saltstone grout to be disposed of on-site; treated water to be released to the environment; and organics to be incinerated. The tanks used for storage of the wastes, after being emptied and washed, will be decommissioned in compliance with the Federal Facility Agreement (FFA).

The processes involved in the HLW complex at SRS are waste generation, storage, evaporation, sludge processing, salt processing, waste water treatment, vitrification, and solidification. These processes involve detailed chemical operations and take place at the specific process facilities designed for each operation. The facilities are Waste Canyons, Tank Farms, Evaporators, Extended Sludge Processing (ESP), In-Tank Precipitation (ITP), Late Wash (LW), Saltstone, Defense Waste Processing Facility (DWPF), and Effluent Treatment Facility (ETF). A brief description of the physical and chemical process involved in each facility is provided in Sections III.A. through III.I. Each of these process steps is modeled to varying degrees by the ProdMod simulator.

III.A. Waste Generation

The liquid waste is made up mainly of many waste streams generated during recovery and purification of transuranic products and unburned fissile material from irradiated fuels, targets, and blankets. The separations are performed in the F- and H-Canyons. A small amount of liquid waste is also generated from the site test and research laboratories. A significant amount of low level waste is generated as a by-product during waste processing operations.

III.B. Waste Storage

The generated liquid waste is stored in F- and H-Area Tank Farms. The SRS has a total of 51 tanks, with tanks numbering 1 through 51, ranging in volumetric capacity from 0.75 to 1.3 million gallons. The F-Area Tank Farm has 22 tanks, and the remaining 29 tanks are in H-Area. Of these 51 tanks, two tanks have been decontaminated and decommissioned. All these tanks are carbon steel walled, inside a reinforced concrete containment vault, and consist of four designs known as Type I, Type II, Type III, and Type IV. The following tanks in H-area are reserved for special purposes in the waste processing operations: Tanks 22, 48, and 49 for ITP; Tanks 40, 42, and 51 for ESP; Tank 50 for spent wash water storage.

III.C. Waste Transfer

The supernate, sludge, and dissolved salt are removed from the waste tanks through underground waste transfer lines to the pretreatment facilities in preparation for final disposal. The supernate is simply decanted using transfer pumps. Water is added and slurry pumps are started to dissolve the saltcake; the dissolution ratio is typically 2 parts water to 1 part saltcake. Water is also added and slurry pumps are used to agitate the sludge. The dissolved salt and the agitated sludge are then moved using transfer pumps to the ITP and ESP, respectively. Once waste from a tank is transferred, the tank is washed with wash water and the contaminated tank wash water is then processed as HLW.

III.D. Evaporation

The liquid wastes are reduced to about 30% of the original volume in a concentrated solution containing most of the radionuclides which finally crystallizes into an immobilized salt known as saltcake. The remaining watery portion of the supernate resulting from evaporation is called the overhead. The overhead, after passing through the mercury collection tank, is passed through an ion exchange column to remove residual Cs^{137}. The concentrated evaporator bottoms cool after coming to the evaporator receipt tank, crystallize into solid salt with interstitial supernate and deposit on the tank bottom. The concentrated salt solution left on the top of the solid salt is transferred back to the evaporator feed tank for further evaporation. Each evaporator has a designated feed tank and can select a receipt tank from its designated drop tanks. The drop tanks are reserved and selected by an evaporator as a receipt tank only if there is space available in the tank. The site has two evaporators (2F and 2H) now in operation, one in each Tank Farm. Construction has been completed on a third evaporator, the Replacement HLW Evaporator (RHLWE), which is to begin hot operations in October 1999.

III.E. Waste Water Treatment

The Effluent Treatment Facility (ETF), located in the H-Area, treats the waste water through a series of processes including pH adjustment, sub-micron filtration, heavy metal and organic removal, reverse osmosis, and ion exchange. The influent in ETF comes from evaporator overheads, segregated cooling water, contaminated surface water runoff, and transfer line catch-tank streams. The clean, treated effluent is discharged to a permitted on-site outfall, and the contaminated effluent, after being reduced in volume, is processed again as HLW. In ETF, the waste water influent is pH adjusted to maximize solids removal in the filter system. The sub-micron filtration process removes suspended solids; the filters are cleaned with oxalic acid, caustic, and chlorine. The feed is treated with $Al(NO_3)_3$ and/or $Fe(NO_3)_3$ to reduce filter fouling. Reverse osmosis removes dissolved salts, and the mercury and Cs^{137} removals are performed by ion exchange.

III.F. Sludge Processing

The sludge from the HLW tanks is processed at the Extended Sludge Processing (ESP) Facility in H-Area in several batches. Sludge processing is a major operation, which consists of aluminum dissolution and sludge washing. Part of the sludge inventory contains large amounts of aluminum, which is dissolved by heating the sludge in high caustic concentration at an elevated temperature (60 ^oC). The dissolution process converts about 75% of the insoluble Al_2O_3 -(3)H_2O (gibbsite) and $Al(OH)_3$ into soluble form according to the following stoichiometries:

$$Al_2O_3 + 3(H_2O) + 2NaOH = 2NaAl(OH)_4$$

$$Al_2O_3 + 3(H_2O) + 2NaOH = 2NaAlO_2 + 3H_2O$$

$$Al(OH)_3 + NaOH = NaAl(OH)_4$$

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$

Some aluminum present as Al_2O_3 -(1)H_2O (beohmite) and aluminum-silica compounds is not soluble at ESP's dissolution temperature. The aluminum is removed to decrease the required ratio of frit to waste in order to have good quality glass and reduce the number of glass canisters produced. The supernate containing dissolved aluminum is then decanted. The settled sludge contains a significant fraction of interstitial supernate containing a large amount of dissolved sodium salts ($NaOH$, $NaNO_3$, $NaNO_2$, $NaAlO_2$, Na_2CO_3, Na_2SO_4, etc). The soluble salts are removed by repeated washing with a low salt content wash water until a sufficiently low sodium concentration is achieved. If the salts were not removed, the vitrification process would again require a larger frit to waste ratio to make good glass, which would ultimately increase the number of canisters produced.

III.G. Salt Processing

Salt processing is another major operation in HLW treatment that was to take place in the In-Tank Precipitation (ITP) Facility in H-Area in batches like ESP. In this process, the dissolved salt from the HLW tanks are separated into two streams: a highly radioactive portion called the precipitate slurry and a low level radioactive portion called the decontaminated filtrate. The soluble cesium is precipitated with sodium tetraphenylborate (NaTPB) and the strontium, uranium, and plutonium are adsorbed on monosodium titanate (MST) to form insoluble solids. The non-radioactive potassium and ammonium are also precipitated. The potassium ion concentration is 100 times that of the cesium concentration. The stoichiometries for the precipitate forming reactions are as follows:

$$CsNO_3 + NaB(C_6H_5)_4 = CsB(C_6H_5)_4 + NaNO_3$$

$$KNO_3 + NaB(C_6H_5)_4 = KB(C_6H_5)_4 + NaNO_3$$

$$NH_4NO_3 + NaB(C_6H_5)_4 = NH_4B(C_6H_5)_4 + NaNO_3$$

Among all TPB compounds, the NaTPB is appreciably soluble in water. The resulting precipitate and the adsorbent solids, which contain most of the radionuclides, are concentrated to 10 wt% precipitate slurry using crossflow filtration. The filtrate is sent to the solidification process in Saltstone. The 10 wt% precipitate slurry at the end of each ITP cycle, which consists of several batches, is repeatedly washed and filtered to reduce its Na^+ concentration to 2 molar. During washing, corrosion inhibitors ($NaNO_2$ and/or NaOH) are added to protect the carbon steel of the ITP tank against corrosion. The precipitate slurry is transferred to the Late Wash Facility, which is a part of the Defense Waste Processing Facility (DWPF).

The partially washed 10 wt% precipitate slurry is again washed in the Late Wash Facility, by dilution and filtration similar to the ITP process, to reduce $NaNO_2$ concentration to 0.01 molar. In the Late Wash, the slurry is reprecipitated with NaTPB to remove the remaining cesium and reconcentrated by filtration. The filtrate, after being chemically adjusted for corrosion inhibition, is transferred back to ITP for reuse.

Based on a recent major redesign study, the ITP process (which was found to generate excessive benzene) is to be replaced by one of two candidate processes currently under evaluation: the Small Tank TPB Precipitation (SMTPB) process or the Crystalline Silicotitanate (CST) Ion Exchange process. The SMTPB process has some aspects that are similar to the ITP process and is the primary candidate to replace ITP, while the CST process is the backup candidate. Since much of the present work was completed prior to the decision to replace the ITP process, the results here will be presented in the context of ITP. The model's general characteristics are in any event independent of the specifics of the replacement process. ProdMod did play a key role in the evaluation of the alternatives to ITP, and that application of the model is described in Section VI.B.

III.H. Solidification

The solidification of the decontaminated salt solution from the Salt Processing facility takes place in the Saltstone Facility, which is a part of the DWPF. In the Saltstone Facility, the salt solution is mixed with a blend of cement, flyash, and blast furnace slag to generate non-hazardous low level waste grout. The grout is then pumped into a large concrete vault divided into a number of cells of equal volume. The grout solidifies into a monolithic, non-hazardous solid waste called saltstone. After filling, the vault will be capped with clean concrete, and the final closure of the area will cover the vaults with a clay cap followed by backfilling with earth.

III.I. Vitrification

The Vitrification Facility is the third element in the DWPF. The DWPF is the largest waste glassification plant in the world and is now operational. In the vitrification process, the washed precipitate from Late Wash and the washed sludge from ESP are mixed with sandlike borosilicate glass called frit to create an immobilized glass solid. The vitrification process includes chemically treating the washed precipitate and sludge, mixing them with a frit, heating the mixture in a melter, and pouring the molten mixture into a stainless steel canister.

The washed and concentrated Cs- and K-TPB precipitate slurry is acid hydrolyzed and steam stripped in the Salt Process Cell. The step removes the aromatic organics from the aqueous stream because a high concentration of organics interferes with melter operation. Hydrolysis is performed using formic acid in presence of copper catalyst according to the following stoichiometric equations.

$$KB(C_6H_5)_4 + HCOOH + 3H_2O = KCOOH + C_6H_6 + B(OH)_3$$

$$CsB(C_6H_5)_4 + HCOOH + 3H_2O = CsCOOH + C_6H_6 + B(OH)_3$$

After aromatic organics are steam stripped, the remaining aqueous phase is known as Precipitate Hydrolysis Aqueous (PHA). In the Chemical Process Cell, sufficient HNO_3 is added to the washed sludge to react compounds such as nitrite and carbonate and to obtain an acidic pH. The PHA is then added to the sludge, and excess water is boiled off, condensed, and collected. The acidified and concentrated sludge and PHA are then mixed with frit, and excess water is again boiled off, condensed, and collected. The mix of sludge, PHA, and frit is required to meet five objectives: 1) glass durability, 2) melt viscosity, 3) melt liquidus, 4) minimum frit, and 5) limits for glass insolubles. The combined sludge, PHA, and frit are then sent to the Melt Cell where the mixture is heated into molten glass. The molten glass is vacuum poured into a stainless steel canister where it is allowed to cool and solidify. After filling, the canisters are cleaned by blasting with a dilute slurry of glass frit followed by rinsing with clean water. The cleaned canisters are then sent to the Glass Waste Storage Building (GWSB) where the canisters are temporarily stored until the Federal Repository is ready.

IV. MODELING ASPECTS

The Production Planning Model (ProdMod)[5,6,7] is a simulation program developed to represent the entire Savannah River Site high level waste complex. ProdMod encompasses all the key processing operations: waste evaporation; saltcake production and dissolution; filtration (dewatering); precipitation; sludge and precipitate washing; glass, grout, and organics production. The major flow streams modeled in ProdMod are shown in Fig. 1. [3] The incoming HLW (stream 1), consisting of supernate and sludge, is stored in the HLW storage and evaporation facility (Tank Farm). The Tank Farm safely stores these wastes until downstream facilities are available for further processing. Most of the supernate is evaporated to solid saltcake to reduce its volume and mobility. The decontaminated overheads from the evaporators are combined with overheads from the separation processes and other low-level streams, and sent to the Effluent Treatment Facility (ETF) (stream 13). The sludges (stream 2) are transferred to the Extended Sludge Processing (ESP) Facility via hydraulic slurrying techniques. In ESP, sludges with high aluminum content are processed to remove part of the insoluble aluminum compounds. All sludges are then washed with water to reduce their soluble salt contents. The spent wash water (stream 3) is sent back to the Tank Farm, while the washed sludge (stream 4) is sent to Vitrification. The sodium-, potassium-, and cesium-rich crystallized saltcake is dissolved with water using hydraulic slurrying techniques. The supernate and/or dissolved salt (stream 5) from different tanks are sent to the In-Tank Precipitation (ITP) Facility (or to its future replacement), where the salt solution is separated after precipitation and filtration steps into a very highly radioactive concentrated slurry (stream 7) for vitrification and a very low radioactive filtrate (stream 6) for solidification. In Vitrification at the Defense Waste Processing Facility (DWPF), the precipitate is catalytically decomposed and separated into two streams: a mildly contaminated organic stream (stream 11), which is sent to the Consolidated Incineration Facility (CIF) for final destruction by burning; and an aqueous stream containing virtually all of the radionuclides, which is combined with the washed sludge from ESP and sent to the glass melter. In DWPF Late Wash, the precipitate is further washed to reduce the level of sodium nitrate and nitrite (which had been added to inhibit tank corrosion) to the levels acceptable by the glass melter. The spent wash water (stream 8) from this process is sent back to the ITP process for reuse. The washed sludge from ESP is chemically adjusted, stripping out a significant amount of mercury (stream 12). The precipitate and sludge are mixed with glass frit and sent to the melter where the wastes are melted into a borosilicate glass matrix, which is poured into a stainless steel canister (stream 9). The water vapor driven off from the melter along with other aqueous streams generated during vitrification are sent back to the Tank Farm for further processing (stream 10). In ETF, the contaminants are separated and sent back to ITP (stream 15) where they are mixed with the decontaminated salt solution from ITP. This mixture of LLW is then sent to the Saltstone Facility (stream 6) where it is mixed with cement former and pumped as a wet grout to a Saltstone Vault (stream 16). In the Saltstone Vault, the grout hydrates and cures, with the vault eventually closed as a landfill. The treated waste water (stream 14) flows to the site water environment.

The waste processing operations are modeled using simple algebraic equations. ProdMod tracks the waste inventory in all waste tanks in the waste processing operations throughout the entire time-span of simulation using mass and volume balances. Three chemical species: Na, K, and Cs are tracked in the facilities' waste streams on an as-needed basis; the presence of these species plays a very important role in the waste processing operations.

IV.A. Methodology

The development of ProdMod had three objectives:

1. To simulate the significant responses of the entire HLW complex over the entire time span of operation necessary to clean up all 51 tanks.
2. To interface the simulation with an optimization scheme which makes optimal operational choices by maximizing or minimizing a single objective function or a set of objective functions combined.
3. To carry out the entire simulation in a few CPU minutes on a workstation.

The typical process lifetime span is about 30 years, but ProdMod may need to analyze a time span of 60 to 70 years to evaluate some hypothetical scenarios.

The path chosen to achieve the objectives outlined above are as follows. The waste processing operations are modeled as simply as possible using algebraic equations. The modeling objective is that the predictions of the simple algebraic equation-based model agree to within 10% of the operational values, if available, or the values predicted by more detailed differential-algebraic models. An innovation in the current approach is to set up the time-dependent dynamic simulation problem as a linear form, which can be solved by the SPEEDUP™ software (see next Section) as if it were a steady state problem. That is, the time dependence becomes implicit within the structure of the equations. This approach allows the equations that describe the dynamic behavior of the SRS high level waste complex to be written as:

$$\boldsymbol{F(x)} = \mathbf{0} \tag{1}$$

$$\boldsymbol{x} = [x_1, x_2, x_3, ..., x_n] \tag{2}$$

where, $\boldsymbol{x}$ is a real vector of dimension n and $\boldsymbol{F}$ is a real valued vector function of dimension m ($m \leq n$). The values of m and n depend on the physical model of the complex. In order to solve Eqn. 1 as a set of algebraic equations, a set of n - m specifications of the form:

$$\boldsymbol{Mx} = \boldsymbol{w} \tag{3}$$

is imposed on Eqn. 1 based on the physical nature of the complex modeled. Here, $\boldsymbol{M}$ is a (n - m) x n matrix such that its elements M_{ij} have the properties:

$$M_{ij} \ \varepsilon \ \{0,1\} \tag{4}$$

$$\sum_{j=1}^{n} M_{ij} = 1 \quad \text{for} \quad i = 1, 2, 3, ..., n - m \tag{5}$$

and $\boldsymbol{w}$ is a real vector of dimension n - m. The mathematical construct for the pseudo-dynamic simulation has the following functional form:

$$x_i\,(t+d) = x_i\,(t) + f(t+d,t) \tag{6}$$

where, $x_i(t+d)$ and $x_i(t)$ are the values of a variable at times $t+d$ and t. $x_i(t+d)$ and $x_i(t)$ are simply defined as two different elements (say, x_j and x_k) of the vector $\boldsymbol{x}$ in Eqn. 2, thus the time dependence is only implicitly defined by the form of the equations. Although $x_i(t+d)$ can be considered a future variable while $x_i(t)$ is the current variable, the time step d is never explicitly defined within the equation set. The f is an algebraic function of the problem variables (i.e., elements of $\boldsymbol{x}$) at current and future times and is defined in terms of the implicit time step. In Eqn. 1, the vector $\boldsymbol{x}$ comprises all variables over the entire time span of simulation and the vector $\boldsymbol{F}$ comprises all the linear and nonlinear algebraic equations. The matrix $\boldsymbol{M}$ represents the (n - m) known variables whose values are specified in single variable equation form, and $\boldsymbol{w}$ represents the column matrix of n - m assigned values. The entire construct appears to the solver to be a system of algebraic equations, identical in form to those defining a steady-state condition, for which the solver has a very efficient algorithm.

In ProdMod, t and d in Eqn. 6 are used as integer variables, such as month, year, batch, or cycle number. The ProdMod architecture allows the models to be expanded easily to span varying simulation time horizons. For example, within the SPEEDUP syntax the number of cycles or the number of batches in each ITP cycle, or the number of years spanning a simulation can be varied by simply changing their values in a few locations, which are then used globally. In some instances, simple changes in the model equations may be necessary. Different time scales in time-space can also be used as necessary. For example, the first four years of the simulation may produce monthly results (i.e., the implicit d is one month), while the remainder of the solution produces annual results (i.e., the implicit d in that subset of Eqn. 2 is one year). In effect, the equation set itself is as much the input to the simulation as the constants representing the processes.

Eqn. 7 provides an example as to how the functional forms given by Eqn. 6 are written in SPEEDUP syntax. Eqn. 7 calculates the Na concentration of precipitate slurry in the ITP process (*conc_na_t48_slurry*) before filtration. Another similar equation would define the updated slurry volume (*t48_slurry_vol*). The SPEEDUP translator will expand the equation into *NBATCH* equations to represent all ITP batches in all cycles. This example shows how the future (*index*+1) event-space variables are connected to the present (*index*) event-space variables in the linear form. The same form can be used to represent equations in time-space by running *index* from 1 through *MONTHS* (the number of months spanning the simulation).

```
?REPEAT
   t48_slurry_vol(?(index+1)) * conc_na_t48_slurry(?(index+1)) =
     t48_slurry_vol(?(index)) * conc_na_t48_slurry(?(index)) +
       feed_soln_vol(?(index)) * conc_na_feed(?(index)) +
         dilution_vol(?(index)) * conc_na_dil(?(index)) +
           tpb_vol(?(index)) * conc_na_tpb +
             titananate_vol(?(index)) * conc_na_titanate ;
 ?WITH index  = <1:NBATCH>                                          (7)
```

Another novel aspect of ProdMod is its mapping of process variables from event-space to time-space, and vice versa, in order to couple discrete event processes to continuous processes:

$$x_r(t) \text{ <--------> } x_s(n) \tag{8}$$

where $x_r(t)$ is a process variable in time-space, say the t-th month. $x_s(n)$ is another process variable in event-space, say the corresponding n-th cycle or batch. $x_r(t)$ and $x_s(n)$ are two different elements of $\boldsymbol{x}$ in Eqn. 2. The mapping is done using SPEEDUP Procedures, and allows batch and continuous processes to be simulated simultaneously. The following is an example in SPEEDUP syntax of a call to a Procedure:

```
(vol_out)  SYNKRO  (time,pause_time1,feed_x,flowrate_feed,mon_last,ncycley,
```

nbatchy1,*nbatchy2*,*nbatchy3*,*nbatchy4*,*nbatchy5*,
nbatchy6,*nbatchy7*,*nbatchy8*,*nbatchy9*,*nbatch10*) (9)

In the above SYNKRO procedure call, the event-space parameters *feed_x* and *time* are passed to the procedure, in addition to the number of cycles and the number of batches in each cycle. The procedure returns the time-space parameters *vol_out*. The Procedure SYNKRO is written in FORTRAN and linked with the remainder of the SPEEDUP model to perform the mapping.

ProdMod was fundamentally designed to simulate a complex dynamic system as a pseudo-dynamic problem, which can be solved very rapidly by SPEEDUP as a steady state problem. The pseudo-dynamic problem formulation has an additional key advantage: it makes it possible to easily couple the fast running simulation code with an external optimization algorithm. The details of the optimization algorithm and its successful implementation will be described in another paper currently under preparation.

IV.B. Modeling Platform

ProdMod has been developed using the SPEEDUP™ software package[8], a product of Aspen Technology, Inc. SPEEDUP is a comprehensive simulation software development package implemented in a flowsheeting environment for steady-state and dynamic problems. Unit operations are described within the SPEEDUP syntax using equations, functions, procedures, and logical constructs. If the unit operations can be expressed in simple equation form, then the SPEEDUP syntax provides an efficient way to write those equations directly in the Model section. On the other hand, procedures written in FORTRAN are found to be the most efficient way to model a unit operation which requires calculations involving DO loop constructs, single branch IF tests, integer arithmetic, etc. The operational units are connected in the Flowsheet section by properly connecting the input and output streams among the units. In the Global section, parameters are also linked between two units through equations explicitly defining the identity condition. The initial values and other model input parameters are provided as user input in a structured form for each independent unit in the Operation section. SPEEDUP's Report section is useful in presenting the results in summary form. The SPEEDUP source code can be linked with customized FORTRAN subroutines through its External Data Interface (EDI) features. The EDI features are extensively used in modeling batch processes to allow the passing of parameters between the SPEEDUP models and the customized FORTRAN routines. An independent customized FORTRAN program can also invoke a SPEEDUP-generated executable and pass parameters back and forth. In that case the FORTRAN program acts as a driver to control the simulation.

SPEEDUP translates the user input and the equation set written in SPEEDUP syntax plus the user supplied FORTRAN in Procedure and Function sections, automatically generates its own FORTRAN code, compiles all the FORTRAN, links all necessary object modules, creates an executable, and then generates the solution. During translation, SPEEDUP detects any syntax errors, while any compilation errors in the user FORTRAN and SPEEDUP-generated FORTRAN codes are detected by the compiler. After successful translation, SPEEDUP's steady state solution method (since the ProdMod equation set is so structured) uses block decomposition to break up all the equations into a number of blocks, which are solved sequentially and independently. The decomposition technique reorders the system of equations into a block-triangular form.

The block decomposition is done by two routines: 1) the Harwell MC21 routine[9] is used to obtain a diagonal free from zeros, 2) the Tarjan algorithm[10] is used to reduce the matrix to block lower triangular form. A Jacobian matrix known as the solution matrix is derived from the equations representing the physical processes. Eqn. 1 can be written in Jacobian form:

$$\boldsymbol{J}\boldsymbol{x} = \boldsymbol{b} \tag{10}$$

$$j = \frac{\partial F}{\partial x} \tag{11}$$

where $\boldsymbol{J}$ is the Jacobian matrix of dimension m x m, and $\boldsymbol{x}$ and $\boldsymbol{b}$ are column vectors of dimension m. In the ProdMod application, the Jacobian is a large sparse matrix. The block decomposition analysis breaks the solution matrix into sub-matrices, and displays system size, number of blocks, and maximum block size. The system size is the number of equations (or unknown variables), the number of blocks is the number of sub-matrices, and the maximum block size is the number of equations in the largest sub-matrix (or block). The decomposition creates many one-dimensional linear and nonlinear equation blocks that can be solved directly, and a lesser number of blocks with a system of linear and nonlinear equations that must be solved iteratively. A procedure call is represented by an equation of the form:

$$\boldsymbol{x_k} = f(\boldsymbol{x_l}) \tag{12}$$

where, $\boldsymbol{x_k}$ and $\boldsymbol{x_l}$ are the input and output vectors of the procedure. The vectors $\boldsymbol{x_k}$ and $\boldsymbol{x_l}$ are two different subsets of $\boldsymbol{x}$ in Eqn. 2. A discontinuous function represented by an IF-THEN-ELSE condition can be written in the following general form:

IF ($f(\boldsymbol{x_p}) > 0$) THEN
    $f(\boldsymbol{x_q}) = 0$
ELSE
    $f(\boldsymbol{x_r}) = 0$
ENDIF (13)

where $f(\boldsymbol{x_p})$ is an expression involving a vector $\boldsymbol{x_p}$; $f(\boldsymbol{x_q})$ and $f(\boldsymbol{x_r})$ are algebraic equations containing vectors $\boldsymbol{x_q}$ and $\boldsymbol{x_r}$. The vectors $\boldsymbol{x_p}$, $\boldsymbol{x_q}$, and $\boldsymbol{x_r}$ are three different subsets of the system variables vector $\boldsymbol{x}$ in Eqn. 2. In SPEEDUP, Eqn. 13 is treated as a system of nonlinear equations. SPEEDUP translates this equation into a single equation for each function $f(\boldsymbol{x_p})$ which contain $\boldsymbol{x_p}$, $\boldsymbol{x_q}$, and elements of each function $f(\boldsymbol{x_p})$. The derivatives of Eqn. 13 reflect those variables that are present in the currently active branch. Those that are not present, simply have zero derivatives.

SPEEDUP then solves each of the diagonal blocks independently and sequentially. The one dimensional linear equations can be trivially solved, while the system of linear equations are solved using LU decomposition with pivoting.[11] The nonlinear equations are solved using the Newton method with some variation.[11] Fig. 2 describes the sequences that take place in performing simulations with the SPEEDUP package. A detailed discussion of the solution techniques in SPEEDUP for steady-state and dynamic simulation is provided by Patalides.[12]

IV.C. ProdMod Development

ProdMod models the entire SRS HLW complex using standard SPEEDUP sections: Title, Option, Declare, Model, Procedure, Function, Global, Flowsheet, Unit, Operation, and Report. Twenty five waste complex unit operations are modeled by 23 models. The replication feature in SPEEDUP allows more than one unit operation to be described by a single model as long as the equations describing the process operations are identical. The parameters in the unit operations may be different, and these parameters are separately passed to each identical unit operation. Twenty six Procedures are used to describe the details of unit operations, and are invoked by the SPEEDUP models in a subroutine form. SPEEDUP's Report features are extensively used in presenting ProdMod results in summary form.

The ITP and ESP are both operations within which the materials are processed in defined batch and cycle steps. The ESP and ITP have been described in Section III. These two processes are modeled in discrete event-space rather than time-space, and these processes are connected with other continuous processes through the incoming and outgoing streams via the mapping feature. The continuous processes operate in time-space on a monthly or an annual basis. The incoming streams to the ITP and ESP processes are mapped into the event-space from the time-space, and the outgoing streams are mapped back into the time-space from the event-space. The ITP (or its replacement process) and ESP operations are the key to determining both the amount and quality of glass canisters produced and the timings when these glass canisters are produced. Hence, these models are simulated in significant detail in ProdMod. The current ProdMod structure can handle 20 ITP cycles and in each cycle there are a number of user specified batches. In each batch, a specified amount of salt solution is fed into an ITP tank from a few selected tanks. A specified amount of spent wash water (if available) is added to the salt solution. A calculated amount of dilution water is then added if the Na concentration of salt solution plus spent wash water exceeds a user specified value.

The precipitating and adsorbent reagents NaTPB and MST are then added. In the ITP model, the solubility of NaTPB in water and the complex nonlinear behavior of the reaction rate dynamics of NaTPB with Cs, K, and NH_4 nitrates are modeled by simple correlations. In ProdMod, the amount of NaTPB added is assumed to be 110% of the stoichiometric value determined by the concentrations of K^+ and Cs^+ in the salt solution. The amount of MST needed depends on the concentration of Sr, U, and Pu in the salt solution, but ProdMod uses a correlated value of 0.3 gm of MST per liter of salt solution. After precipitate is formed, the precipitate slurry is concentrated to 10 weight percent (wt%) solids by dewatering through crossflow filtration. The batch operations in producing precipitate are repeated until all batches in a cycle are complete. At the end of the batches, the 10 wt% precipitate slurry is partially washed with water to lower Na concentration, and during washing corrosion inhibitors NaOH and $NaNO_2$ are added. In the ITP model, the Cs concentration in the precipitate slurry is also tracked so that it does not exceed the operating limit based on shielding design.

ProdMod models ESP's two important processes: aluminum dissolution and sodium washing (see Section III.F.). The sludges with high aluminum are sent after aluminum dissolution for sodium washing along with other sludges. The sludges are washed as batches in two ESP tanks, and each sludge batch consists of sludges taken from a selected number of tanks. At the end of sludge washing, when one tank is busy in transferring sludges to the vitrification process, the sludge washing progresses in the other tank. The washes are performed in cycles and the number of wash cycle steps can be defined arbitrarily by the user. The model is set up to terminate the wash automatically when the washing criterion is met, assuming the maximum number of cycles allowed is not exceeded.

Three evaporators, 2H, 2F, and RHLWE (Section III.D.) are modeled in ProdMod using a similar equation subset, but each evaporator model has its own specific tanks associated with it. Each evaporator has a designated feed tank and selects a receipt tank from its designated drop tanks. The drop tanks are reserved and selected by an evaporator as a receipt tank only if there is space available. If a tank is not selected as a receipt tank, within that tank the supernate can be decanted or the saltcake can be dissolved for transferring to the ITP tank. A few tanks are also assigned to each evaporator as the waste storage tanks, and the wastes from these tanks are transferred to the evaporator feed tank at a later date for evaporation. In ProdMod, the evaporator model drives off excess water as the overhead, and the rest concentrates as the saltcake in the receipt tank. The splitting fractions used to determine the overhead and the concentrate are based on evaporator operating data and differ for different types of waste. In actual operation, the evaporator overhead is a function of the specific gravity of the feed, and the supernate from the top of the saltcake is recycled back to the feed tank. The evaporator models also track the space available and the inventory of all tanks associated with the evaporator system. The evaporator models perform salt dissolution in the salt tanks using Procedure calls. A fraction of the saltcake is trapped sludge, and the evaporator model tracks that sludge. The trapped sludge is finally processed with the settled sludge in the ESP facility. The tank inventory and salt dissolution in those tanks in F- and H-Area which are not associated with an evaporator system are modeled by F- and H-Area waste removal models, respectively.

The ETF (Section III.E.) is modeled as a volume balance with a stream splitter. The five input streams supply the incoming volume (on a monthly or an annual schedule) which is split according to a user supplied split ratio. The split ratio can be time dependent. The model then calculates the treated outfall and concentrated volume as its output streams.

The Late Wash facility (Section III.G.) is represented as a volume balance and precipitate washing model. The Late Wash model receives precipitate from the ITP unit operation and washes the precipitate to reduce the $NaNO_2$ level to 0.01 molar, which is equivalent to 0.09 molar Na^+ concentration. The washed precipitate is then supplied to the DWPF model to meet its input demand. The spent wash water from this model is stored in a tank to supply dilution water in the ITP model on demand.

In the Saltstone model (Section III.H.), the volume of grout produced is proportional to the decontaminated filtrate volume in. The proportionality constant is a time dependent (on a monthly or annual schedule) user input and is currently set based on operating data. The masses of cement, slag, and flyash are modeled as proportional to the volume of decontaminated salt solution. The proportionality constants are also time dependent user inputs and are currently based on operating data. The Saltstone model tracks vault storage inventory using a Procedure call.

A simplified DWPF model (Section III.I.), based on a very complex model CPES (Chemical Process Evaluation System),[13] is implemented in ProdMod. The model calculates the number of glass canisters produced depending on the user specified attainment and nominal glass mass production rate. The model calculates the required precipitate, sludge, frit, and hydrolysis water using a mass balance based on the complex chemical composition of sludge, precipitate, and frit. The precipitate and sludge are the input streams coming from the Late Wash and ESP models respectively. The model also calculates the recycle water and organic waste streams. The recycle water stream is calculated from the mass balance of aqueous precipitate and sludge, hydrolysis water, and all other water added during the vitrification process. The model also adds corrosion inhibitors (NaOH, $NaNO_2$) to the recycle stream to meet the required specification.

A 30-year simulation of the entire SRS HLW complex requires 75,006 equations to be solved for the unknown variables. The total system size, which includes both known and unknown variables, is 88,220. The equations are broken into 67,113 independently solvable blocks, and among these blocks there are 67,029 single equation blocks. The maximum block size, i.e., the highest number of equations in a single block is 1124, and there are 3,205 nonlinear blocks. An equation represented by a conditional statement, IF–THEN-ELSE, is considered a nonlinear equation within the SPEEDUP structure. ProdMod is routinely executed on an IBM RS/6000 Model 560 platform. The run time for a 30-year simulation of the entire waste complex is about one CPU minute on this platform. ProdMod is directly portable to the Cray and VAX computer platforms.

V. MODEL VALIDATION

The models in ProdMod have been developed based on facility design parameters and correlations based on laboratory experimental data and facility operational data. Limited amounts of operating data are available because some facilities are not yet in operation and others have not been in operation for long.

For the ITP process, no operational data are available (as discussed in Section VI.A, that process will be replaced in the future). Thus for validation of ProdMod, its predicted ITP results have been compared against an independent calculation performed by other researchers.[14] The comparative results are presented in Table IV. The ProdMod analysis assumed an addition of 110% of stoichiometric NaTPB in all batches, whereas the independent calculations were based on an addition of 150% of stoichiometric NaTPB in the first batch of each cycle and 100% in subsequent batches. The amount of precipitate produced in a batch is related to the amount of NaTPB added in a batch. The NaTPB values and the corresponding precipitate productions in Table IV under column "Independent Calculations" have been adjusted to 110% of stoichiometric NaTPB for a consistent comparison basis. Table IV shows that the results predicted by ProdMod agree fairly well with the independent calculations, except for the dilution water data. For dilution water calculations, ProdMod and the independent calculations used different scenarios for the water sources, which resulted in the use of water of different Na concentrations. The effects of these two different bases impact the results in some batches. As an example, the dilution water addition predicted by ProdMod in Batch 1 of Cycle 1 is 35,000 gal, whereas no dilution was needed for the independent calculation case.

In evaporator operations, the specific gravity of the concentrate is maintained at a constant value. Hence, the split of the waste solution between the overhead and the concentrate streams depends on the specific gravity of the waste solution. In ProdMod, the evaporators are modeled as splitters with a splitting coefficient that depends on the source of the waste. The splitting coefficient is termed the space gain factor (sgf). The sgf fraction of the waste goes to the overhead, and the remaining (1-sgf) fraction accumulates as salt in the evaporator drop tank. The sgf values are related to the sources of waste generation. In ProdMod, these sgf values are subject to change by the user. The default values are replaced as the latest facility data become available.

The ESP results predicted by ProdMod have been compared against the detailed steady state CPES[13] computer code. The comparative results are presented in Table V. The volumes of sludge processed having a specified weight percent of dry solids for five sludge batches, after aluminum dissolution (if necessary) and salt washing to a specified amount of Na molarity, are compared. Table V shows that the ProdMod-predicted processed sludge volumes are significantly higher in three batches. This discrepancy can be addressed appropriately once the operating data are available and the ESP models are validated. Only one ESP batch had been processed so far in the ESP facility. The other important parameter, the sludge loadings per 200 canisters predicted by ProdMod are in excellent agreement with the CPES results.

The Saltstone and DWPF models have been developed based on the design parameters, but the model predictions are found to be in good agreement (within 10%) with the recently available facility data. The Saltstone and DWPF model predictions for various production quantities, along with the corresponding operating data, are presented in Table VI.

VI. CASE STUDIES

Results predicted by ProdMod are being used routinely at the SRS in developing operational plans and strategies. In addition, ProdMod has also been used in studying variations in existing processes, as well as entirely new processes proposed for the HLW complex. Such applications are described in this section.

VI.A. Process Variations

ProdMod has been used in studying alternative processing choices. Tables VII and VIII summarize two such applications. Table VII shows a comparative study of three different cases for washing precipitate in which: A) all Na washing is performed in ITP, B) all Na washing is in Late Wash, and C) the washing is split, partly in ITP and partly in Late Wash. In Case A, spent wash goes directly to Saltstone for grout formation; the spent wash water can not be re-used for dilution water due to logistical problems. The spent wash water from Late Wash in Case B is logistically permitted to be used for dilution water in ITP. In Case C, the spent wash water from ITP goes to Saltstone directly, but the spent wash water from Late Wash can be used as dilution water in ITP. For Case C, the Na concentration in spent wash water from Late Wash is much lower than that in Case B. The Na concentration in Late Wash spent wash water in Case B comes from precipitate washing from 5 molar to 0.09 molar, whereas in Case C the Late Wash spent wash water Na concentration comes from precipitate washing from 2 molar to 0.09 molar. Hence, the additional inhibited water (0.015 molar Na concentration), if required for more dilution, is much lower in Case C than that in Case B. The additional inhibited water produces additional decontaminated salt solution, and ultimately additional grout and added cost. Hence, among all three choices, the waste production is the lowest and cost savings is the most in Case C. The predicted results are based on 5 years of operation and demonstrate millions of dollars in cost savings and millions of gallons of less waste production from one choice to another. Table VIII shows a comparative study of sludge washing using constant and variable wash water volumes in each cycle. The results show that there is a net reduction of 200,000 gal of spent wash water over five cycles in washing the sludge batch from an initial 0.192 solid Na weight fraction to a set limit of 0.09 solid Na weight fraction for the variable wash water volume case. The washing of sludge to 0.09 molar Na concentration is required to produce the optimum amount of glass waste while maintaining optimum glass quality.

The production of precipitate in ITP (or whatever process replaces it) is an important operation in the SRS waste processing complex. Precipitate production is associated with many important factors that play key roles in the management of HLW. Table IX presents the results of four ITP batches in a cycle. The table shows: 1) the amount of waste processed, 2) the needed quantity of NaTPB (an expensive item to purchase), 3) the volume of dilution water needed, 4) the amount of decontaminated salt solution produced (filtrate) for Saltstone, 5) the quantity of spent wash water generated, and 6) the amount of 10 wt% precipitate slurry produced. At the end of all batches in a cycle, the precipitate is washed. Table IX also shows the required quantities of wash water and corrosion inhibitors (NaOH and NaNO2), the amount of spent wash water generated, the amount of precipitate available to transfer, and the Cs loading in the processed precipitate slurry. The parameters in Table IX play an important role in guiding the planners in operating the ITP facility.

ProdMod has been applied in evaluating different planning scenarios. A few of these are: operating the Vitrification Facility at different DWPF attainments, different ITP and Late Wash start dates, the permanent shutting down dates of the evaporators. The annual glass production rate which consumes processed precipitate, sludge, and frit at two different DWPF attainments is shown in Table X. This type of study is important in meeting the regulatory commitments for cleaning the tanks before an agreed deadline and also having the required resources ready on time.

VI.B. Salt Disposition Alternatives Study

Most recently, ProdMod has played a key role in the Salt Disposition Alternatives (SDA) task, whose goal is to select and design a salt processing alternative to the current ITP process which has been found to produce excessive benzene. For Phase III of the SDA task, four proposed alternatives (which had been selected out of a group of 18 earlier alternatives) were to be evaluated in order to select a primary choice and a backup. The four alternatives were: Cesium Encapsulation in Grout, Small Tank TPB Precipitation, Crystalline Silicotitanate (CST) Ion Exchange, and Caustic-Side Solvent Extraction. The function of ProdMod was to develop a workable scenario for the implementation of each alternative, ensuring that the specifics of each alternative would integrate properly with the ongoing HLW operations. Based on the unique time-line determined by ProdMod for each of the four alternatives, the time-varying feed composition for each alternative was determined and subsequently used in much more detailed process unit operation models. The selection of the two alternatives advancing to the next round of evaluation was then based on detailed process evaluations, cost factors, and measures of technical risk.

ProdMod modeled the Cesium Encapsulation in Grout option under the assumption that the new grout facility will be in operational in March 2006, and will begin processing at maximum throughput. The DWPF production rate of 235 canisters per year is synchronized to the Grout Facility production rate so that both the facilities can cease their operations at the same time. As a result, all the MST that has adsorbed Sr, U, and Pu, plus the residual sludge solids, can be transferred periodically to the sludge feed in DWPF. The DWPF recycle to the Tank Farm is based on sludge-only operation. After meeting the regulatory commitments and the operational constraints, ProdMod scheduled the salt solution blending such that the Tank Farm provides 6.44 million gallons of salt solution at the 6.0 molar Na condition, with less than 3 Ci/gal Cs contents, to the proposed new Saltstone facility. The modeling results indicate that salt processing via Cesium Encapsulation in Grout would complete in FY 2018, along with sludge-only glass production completion at the same time.

In modeling the Small Tank TPB Precipitation option, it was assumed that the new facility is ready for operation in May 2006. The Tank Farm provides a blended salt solution of 5.2 million gallons at 6.44 molar Na per year on average, which produces approximately 325,000 gal 10 wt% precipitated slurry without exceeding the Cs concentration limit of 46 Ci/gal. The salt solution is diluted to 4.7 molar Na in the new Small Tank Facility before adding precipitating reagents. ProdMod modeled the precipitate production rate with a 120% of stoichiometric NaTPB addition based on the K and Cs present in the salt solution, along with MST adsorbents for Sr, Pu, and U. The available spent wash water from precipitate wash was used for the required dilution water. The DWPF recycle volume to the Tank Farm was based on sludge-only operation before the Small Tank Facility start-up, and after the start-up an additional 320,000 gal/year was added. ProdMod modeled the DWPF canister production rate at 210 cans/year in DWPF so that the sludge and precipitate processes finish their feeds to DWPF at the same time. Modeling results indicate that salt processing via the Small Tank TPB option would complete in FY 2020, which also corresponds to the end of sludge processing.

ProdMod modeling of the CST Ion Exchange option is based on the new facility start-up date in March 2007. In this option, the Tank Farm provides a blended salt solution of 6.0 million gals at 6.44 molar Na per year on average, which does not exceed the K and Cs limits of 0.173 molar and 3.30 Ci/gal respectively. The salt solution is then diluted to 5.6 molar Na in the Ion Exchange facility for feed to the Ion Exchange columns. In ProdMod, the contaminated CST production rate is based on a logarithmic correlation. The DWPF recycle volume to the Tank Farm is again based on sludge-only operation algorithm before the new facility start-up, and after the start-up an additional amount of 1.1 times CST production in terms of gal/lb is added. A DWPF canister production rate of 225 cans/year is modeled so that the radionuclide-loaded MST and CST from salt processing can be blended with the sludge at DWPF, and both sludge and salt processing can finish at the same time. It is also assumed that no additional cans will be produced as a result of the blending of CST resin with the sludge feed. ProdMod predicts that salt processing via CST Ion Exchange, together with sludge processing, would complete in FY 2019.

Based on the assumption that the new Caustic-Side Solvent Extraction Facility will start up in May 2007, ProdMod has been used to model and evaluate clean up operations using this salt disposition option. The results indicate that salt processing via Caustic-Side Solvent Extraction would complete in FY 2019, which corresponds to the end of sludge processing in DWPF with a canister production rate of 225 cans/year. That canister production rate is driven by the need to finish sludge processing at the same time as salt processing so that spent MST along with the separated Cs stream from salt processing can be blended with the sludge in DWPF. In ProdMod modeling, it is also assumed that the Solvent Extraction feed to DWPF can be blended in with the sludge feed without an increase in canister production. In this option, the Tank Farm provides a blended salt solution of 6.0 million gals at 6.44 molar Na per year on average, which does not exceed the Cs limits of 4.0 Ci/gal. The DWPF recycle volume to the Tank Farm is based on sludge-only operation before the new facility starts up, and after the facility has started up an additional 520,000 gal/year is added. Based on ProdMod results, both salt and sludge processing would complete in DWPF in FY 2019, while producing 225 cans/year.

The use of ProdMod described above provided significant input to the decision to move forward with the Small Tank TPB Precipitation alternative as the primary option to replace the original ITP process, with the CST Ion Exchange alternative as the backup option.

VII. CONCLUSIONS

A methodology to simulate the dynamics of complex, integrated plant processes efficiently has been developed, using algebraic equations in a pseudo-dynamic form. When the pseudo-dynamic construct (in which the simulation time interval is implicit) is combined with a mapping technique to couple the continuous time-space with discrete event-space, the result is a computational tool which executes rapidly without sacrificing details in discrete event-space. The mapping technique allows the discontinuities (and subsequent computationally burdensome reinitializations) inherent in the dynamic simulation of batch processing to be avoided.

This methodology has been used to successfully develop a fast running simulation code ProdMod to simulate the operation of the Savannah River Site's entire High Level Waste Complex through its entire 30 years of processing in less than two CPU minutes on a work station. The simulation time span can be easily extended to 50 or even to 70 years with minimal effort. The results predicted by ProdMod agree to within 10% with the available operating data. Where operating data are not available, the results predicted by ProdMod have also been compared against independent calculations and found to be in good agreement.

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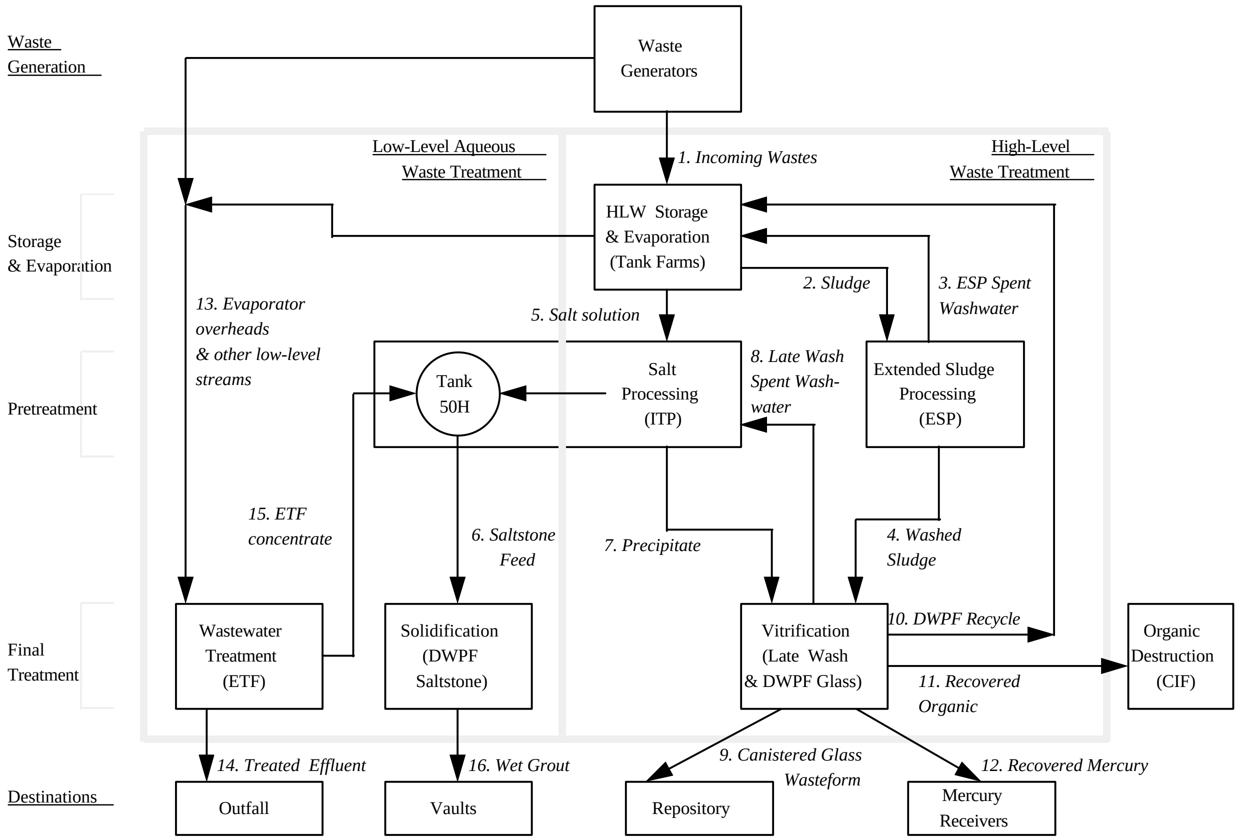

Figure 1. SRS high level waste process flow streams.

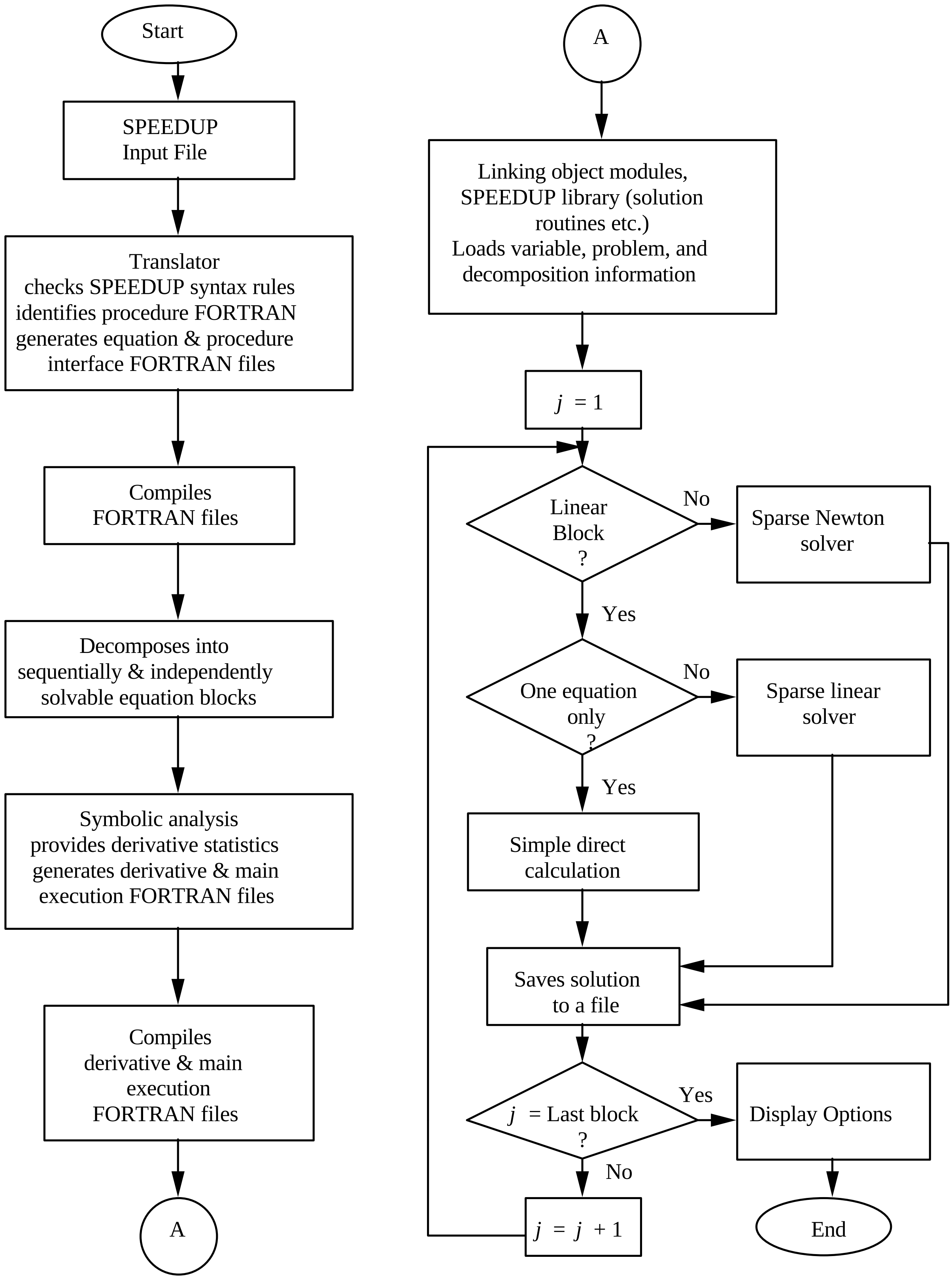

Figure 2. SPEEDUP solution scheme flowchart.

Table I
DOE Managed Nuclear Waste Storage Volumes

Waste Type	Volume (m^3)
High Level Waste	380,000
Transuranic waste	220,000
Low Level Waste	3,300,000
11e(2) Byproduct Material	32,000,000
Mixed Waste	146,000
Other Waste	79,000

Table II
Volume and Curie Content of HLW Among Its Locations

Location	Weapons Related Volume (m^3)	Weapons Related Activity (million Curie)	Non-weapons Related Volume (m^3)	Non-weapons Related Activity (million Curie)
SRS	120,000	490	10,000	42
Hanford	220,000	320	19,000	27
INEL	11,000	52	0	0
West Valley	0	0	2,100	25

Table III
Curie Content and Radionuclide Presence Over Different Time Horizons

Time Horizon	Primary Radionuclides	Weapons Related Activity (million Curie)	Non-weapons Related Activity (million Curie)
0 - 50 Years Half life	Cs^{137}, Sr^{90}, Y^{90}, Ba^{137m}, Pu^{241}	810	90
50 - 500 Years Half life	Pu^{238}, Sm^{151}, Am^{241}	2.7	0.330
500 - 50,000 Years Half life	Pu^{239}, Pu^{240}, C^{14}	0.083	0.0072
Over 50,000 Years Half life	Tc^{99}, Cs^{135}, U^{233}	0.051	0.0045

TABLE IV
Comparison of ProdMod Predicted ITP Results

	Precipitate Production (kgal)		Dilution Water Addition (kgal)		NaTPB Addition (kgal)		Decontaminated Salt Solution (kgal)	
ITP Cycle/ Batch	Indepe-ndent Calcul-ations	Prod-Mod Results	Indepe-ndent Calcul-ations	Prod-Mod Results	Indepe-ndent Calcul-ations	Prod-Mod Results	Indepe-ndent Calcul-ations	Prod-Mod Results
Cycle 1:								
Batch 1	49	59	0	35	34	41	383	394
Batch 2	33	32	40	38	26	23	699	715
Batch 3	58	52	215	226	41	36	642	686
Cycle 2:								
Batch 1	10	13	100	120	9	8	712	741
Batch 2	89	85	500	479	57	56	579	606
Batch 3	6	6	100	126	4	4	670	699
Batch 4	11	12	80	118	8	7	670	715
Batch 5	18	18	75	98	12	12	658	692
Cycle 3:								
Batch 1	7	11	150	155	7	7	765	777
Batch 2	47	45	300	277	31	30	707	710
Batch 3	50	47	275	288	32	32	695	735
Batch 4	29	27	110	161	19	18	659	726
Cycle 4:								
Batch 1	37	38	375	363	26	26	725	748
Batch 2	18	22	200	182	15	14	684	675
Batch 3	25	29	225	261	20	19	702	750
Batch 4	32	34	240	321	23	23	661	758
Batch 5	25	23	140	192	17	15	643	708

TABLE IV (Continued)
Comparison of ProdMod Predicted ITP Results

	Precipitate Production (kgal)		Dilution Water Addition (kgal)		NaTPB Addition (kgal)		Decontaminated Salt Solution (kgal)	
ITP Cycle/ Batch	Indepe-ndent Calcul-ations	Prod-Mod Results	Indepe-ndent Calcul-ations	Prod-Mod Results	Indepe-ndent Calcul-ations	Prod-Mod Results	Indepe-ndent Calcul-ations	Prod-Mod Results
Cycle 5:								
Batch 1	23	26	195	212	18	17	743	782
Batch 2	41	42	280	269	29	28	528	538
Batch 3	19	23	190	186	15	15	683	688
Batch 4	25	23	185	183	17	16	663	674
Batch 5	26	25	140	187	18	17	626	687
Cycle 6:								
Batch 1	43	42	210	217	29	29	341	390
Batch 2	20	23	162	164	17	15	594	606
Batch 3	31	33	325	299	23	23	672	661
Batch 4	30	30	200	289	21	20	374	478
Cycle 7:								
Batch 1	31	30	279	300	21	20	437	488
Batch 2	55	56	325	309	40	38	675	686
Batch 3	23	26	100	157	19	18	629	697
Batch 4	25	27	120	165	19	18	647	704

TABLE V
Comparison of ProdMod Predicted ESP Results

	Processed Sludge Volume			Sludge Loading Per 200 Canisters		
Batch No.	ProdMod Prediction (kgal)	CPES Prediction (kgal)	Difference (%)	ProdMod Prediction (kgal)	CPES Prediction (kgal)	Difference (%)
X1	555	494	12	207	206	0.5
X2	609	621	- 2	207	210	- 1.5
X3	599	570	5	207	216	- 4.2
X4	654	560	17	207	226	- 8.4
X5	877	764	15	207	206	0.5

TABLE VI
Comparison of ProdMod Predicted Vitrification Results

Model Parameters	ProdMod Predictions	Operating Data	Difference (%)
Saltstone Model:			
Dry Materials (flyash, cement, slag), tons (Total in FY 1996)	2,410	2,423	- 0.5
Grout Production (Total FY1990 through FY1996)	3,445	3,764	- 8.5
DWPF Model:			
Canister Glass Mass (lbm) (First 6 canisters)	4,062	4,008	1.3
Recycle Flow (kgal) (October through March in FY1997)	4.3	4.6	- 6.5

TABLE VII
Precipitate Na Washing Choices

Case	Decontaminated Salt Solution (million gal)	Grout Production (million gal)	Relative Cost Savings (million $)
Case A	22.2	35.9	Base Cost
Case B	19.9	32.2	6.13
Case C	18.6	30.2	9.15

Case A : All Na washing (up to 0.09 molar) in Tank 48 in ITP
Case B : All Na washing (up to 0.09 molar) in Late Wash
Case C : Split Na washing between Tank 48 and Late Wash;
up to 2 molar in Tank 48 and to 0.09 molar in Late Wash

TABLE VIII
Sludge Na Washing Using Fixed and Variable Cycle Wash Volumes

	Case A: Cycle End dry Na wt fraction	Case A: Cycle Wash water (kgal)	Case B: Cycle End dry Na wt fraction	Case B: Cycle Wash water (kgal)
Initial dry Na	0.192		0.192	
Cycle 1	0.185	400	0.185	400
Cycle 2	0.153	400	0.153	400
Cycle 3	0.124	400	0.127	350
Cycle 4	0.101	400	0.105	350
Cycle 5	0.082	400	0.089	300
Total Spent Wash Water		2,000		1,800

Case A: Fixed cycle wash water volume
Case B: Variable cycle wash water volume
Initial Na (dry wt solids) - 19.2%
Target Na after washing (dry wt solids) - 9%

TABLE IX
Precipitate Production in an ITP Cycle

Cycle/ Batch Number	Salt Solution	Dilution Water	NaTPB	NaT	Decon Salt Solution	10 wt% Precipitate Slurry
Cycle x	(kgal)	(kgal)	(kgal)	(kgal)	(kgal)	(kgal)
Batch 1	410	305	19.1	1.2	704	33
Batch 2	562	291	11.3	1.4	847	20
Batch 3	430	317	5.0	1.3	744	10
Batch 4	420	345	17.2	1.3	755	29
Total	1,822	1,258	52.6	5.2	3,050	92

At the end of four batches

Wash water added (kgal)	673
NaOH added (kgal)	12
$NaNO_2$ added (kgal)	12
Spent wash water generated (kgal)	697
Precipitate transfer volume (kgal)	92
Precipitate Cs concentration (Ci/gal)	30

TABLE X
Glass Waste Production at Two Different Attainments

	30% DWPF Attainment	50% DWPF Attainment
No. of Canisters Produced	162	270
Precipitate Consumed (kgal)	123	206
Sludge Consumed (kgal)	149	248
Frit Added (kgal)	103	171
Hydrolysis H_2O Added (kgal)	174	290
Recycle H_2O Generated (kgal)	2,431	3,199
Organics Generated (kgal)	15	25